Influence of tetraalkylammonium cations on quality of decatungstate and its photocatalytic property in visible light-triggered selective oxidation of organic compounds by dioxygens

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ABSTRACT

Three decatungstates (DTs) were conveniently synthesized respectively using quaternary ammonium cations of tetramethyl, tetrapropyl and tetrabuthyl as counterions (marked as TMADT, TPADT and TBADT) and their quality, photoluminescence (PL) property and redox capacity were measured by UV–vis, XPS and PL spectra and cyclic voltammograms (CVs), respectively. The photo-catalysis activities of three DTs were checked using visible light-driven selective oxidation of cyclohexane, toluene, ethylbenzene and benzyl alcohol by dioxygens (O_2) in acetonitrile (MeCN). The results showed that the photo-catalysis activity of DT anion for these oxidations gradually increases with the shortening of its cationic alkyl chain, which is attributed to the continuous improvement of its quality from TBADT to TMADT. Furthermore, the additives water, 12 M hydrogen chloride (HCl) solution and especially the mixture of both can markedly promote the DTs-photocatalyzed oxidations and such promotion presents an enhancing trend from TBADT to TMADT. which is likely due to the beneficial effects of these additives as follows: i) Water can significantly stabilize the structure of DT anion under light illumination and improve its redox cycling in MeCN; ii) 12 M HCl may obviously improve the oxidative capacity and redox cycling of DT anion and stabilize its photo-excited states. iii) The respective promotion effects of such two additives on photo-catalysis can be well combined and such combined effect is enhanced drastically upon TMADT owing to its hydrophilic feature, thus significantly improving the photo-catalytic efficiency of TMADT under the joint action of water and 12 M HCl.

1. Introduction

Catalytic oxygenation of hydrocarbons using green hydroperoxide and especially dioxygens (O_2) under mild conditions remains a very important and challenge research field [1]. The oxidation of cyclohexane, as an important commercial reaction, is still a field of ever growing interest [2–4], as its oxygenated products, cyclohexanol and especially cyclohexanone (commonly known as the KA oil), are key intermediates for the production of synthetic fibbers and fine chemicals [5,6]. In industry, cobalt or manganese salts-catalyzed oxidation of cyclohexane by air needs to use the harsh conditions of 423–573 K and 10–20 atm, only providing ca. 4% cyclohexane conversion with less than 75% KA oil selectivity [7,8]. A series of effective catalysis systems have been developed for the molecular oxygen-involved this selective

oxidation [9–18], but most of the above systems always need to employ relatively high temperature and pressure to efficiently activate triplet oxygen molecules.

In developing the molecular oxygen-involved selective oxidation of organic compounds under moderate conditions, the photo-excited polyoxometalates (POMs) show a remarkable catalysis activity for the selective oxidation of a large number of organic compounds, including inactive hydrocarbons [19–26], which should be due to these POMs having the broad range of redox potentials and the reversibility of polyelectron reductions, Among these POMs, decatungstate (DT) anion is one of the most efficient photo-catalysts and has received special attention because of its very important photo-catalytic properties [22,27–30] and its applications in photo-catalysis transformation of organic compounds [31–33] and especially photo-catalyzed oxidation
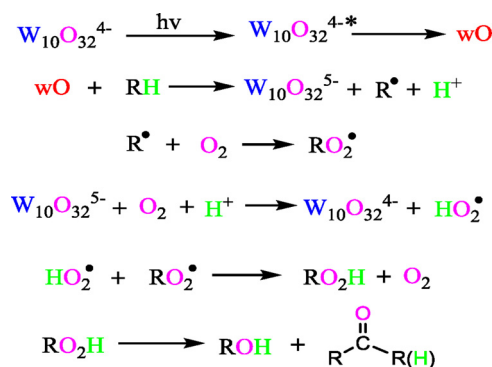
$$W_{10}O_{32}{}^{4-} \xrightarrow{h\nu} W_{10}O_{32}{}^{4-*} \longrightarrow wO$$

$$wO + RH \longrightarrow W_{10}O_{32}{}^{5-} + R^\bullet + H^+$$

$$R^\bullet + O_2 \longrightarrow RO_2{}^\bullet$$

$$W_{10}O_{32}{}^{5-} + O_2 + H^+ \longrightarrow W_{10}O_{32}{}^{4-} + HO_2{}^\bullet$$

$$HO_2{}^\bullet + RO_2{}^\bullet \longrightarrow RO_2H + O_2$$

$$RO_2H \longrightarrow ROH + R\overset{\overset{O}{\|}}{C}R(H)$$

Scheme 1. A generally accepted mechanism for DT anion-photocatalyzed oxidation of hydrocarbons by O_2.

of aliphatic and aromatic alcohols [34–37], alkanes [38–45], and alkenes [46–49]. An important character of DT anion is that it can take place electron transition from its bridge oxygen to tungsten atoms under light irradiation (mainly using UV light), thus leading to the formation of its locally excited state. Such very unstable excited state will rapidly decay in less than 30 ps to a very reactive species with a lifetime of 65.5 ns and a quantum yield of 0.57 (marked as wO) [27,28,30]. Such wO species has a character like oxyradicals owing to the existence of an electron deficient oxygen center [30], so that it can directly oxidize various organic compounds including inert hydrocarbons (RH) to yield its one electron reduced state and a carbon centered radical species (R·) *via* a hydrogen atom abstraction or electron transfer pathway [27–31]. The following re-oxidation of the reduced DT and the formation of the oxygenated products can be achieved under the participation of O_2 (Scheme 1). A number of researchers, triggered by the ongoing interest on DT photo-catalysis, have developed some practical techniques for the improvement of DT-based catalysis systems [30]. For examples, Fe(III) porphyrins as co-catalysts have been used to efficiently promote the tetrabutylammonium decatungstate (TBADT)-photocatalyzed oxidation of cyclohexane [42], cyclohexene and cyclooctene [46] by O_2. In addition, various methods have been developed to prepare the heterogenized DT photo-catalysts, which include that DT is impregnated on solid matrixes [50–52], incorporated into sol-gel network [53–55], bound on silica [56,57], respectively attached to ion-exchange resins [58] or in a polymer membrane [59–61]. These heterogeneous DT photo-catalysis systems are easier to treat and recover catalyst than in a homogeneous DT solution [62,63], but also their photo-catalysis efficiencies are comparable to the corresponding homogenous reaction [33,64]. Notably, we recently found that aqueous hydrochloric acid (HCl) solution as an additive could significantly promote the TBADT-catalyzed selective oxidation of cyclohexane with O_2 in acetonitrile (MeCN) under visible light illumination and thus lead to markedly enhancing cyclohexane conversion (increasing by about 1.5 time) and slightly improving cyclohexanone selectivity, which likely originates from the important roles of such acidic solution in accelerating the photo-redox cycling of TBADT and stabilizing its structure [65].

Some important progresses, as described above, have been achieved in using DT anion to photo-catalyzed the selective oxidation of various organic compounds by O_2. However, to the best of our knowledge, some factors to influence the photo-catalytic performance of DT catalyst are rarely noticed [65,66]. Specifically, some non-photoactive twins such $[W_5O_{16}]^{2-}$ and $[H_2W_{12}O_{40}]^{6-}$ are inevitably produced in the synthesis of the photoactive DT catalyst [19], thus leading to a decrease in the quality or purity of DT catalyst. Furthermore, the conversion of DT catalyst to an unstable subunit $[W_6O_{19}]^{2-}$ in some organic solvents usually occurs under heating [67]. So how to improve the quality of the synthesized DT and its stability in reaction media, closely relative to photo-catalysis, becomes extremely important. Equally importantly, the

strategies to improve the oxidative capacity and redox cycle of DT and to stabilize its photo-excited states are still absent and highly desirable. Herein, we will report the valuable findings in the following two respects: i) How does tetraalkylammonium cation as a counterion affect the quality and redox capacity of the synthesized DT catalyst and its photo-catalytic activity in visible light-triggered selective oxidation of inert hydrocarbons by O_2? ii) It is interesting to further investigate whether the promoted effect of the additive water and especially aqueous HCl solution on the photo-catalytic performance of DT catalyst is affected by these cations and to put forward new opinions for such promoted effect.

2. Experimental

2.1. Materials

Primary reagents used in this work were of analytical grade, which included sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), concentrated hydrochloric acid (HCl), tetramethylammonium bromide (TMABr), tetrapropylammonium bromide (TPABr), tetrabuthylammonium bromide (TBABr), cyclohexane, benzene, toluene, ethylbenzene, benzyl alcohol, acetonitrile (MeCN). Distilled water was used throughout this experiment.

2.2. Synthesis of tetraalkylammonium decatungstate

Referring to our previous work [65], The synthesis of tetraalkylammonium decatungstates is described as follows: 24.25 mmol (8.0 g) $Na_2WO_4 \cdot 2H_2O$ was dissolved with 40 mL of hot water in a 100 mL three-necked flask, the pH value of the resultant solution was adjusted to 1.8–2.5 with 2 M HCl aqueous solution. Followed by that this solution was polymerized at 80–90 °C for 8–15 min under magnetic stirring, the obtained acid type of decatungstate solution was exchanged with 2 M TMABr, TPABr or TBABr solution (4 mL) at 50–80 °C for 20–30 min, thus generating a white or pale yellow solid. After cooling, the obtained solid was filtered, washed with water (10 mL × 3) and acetone (10 mL × 3), and finally dried at 60 °C under vacuum to yield the crude DT salt (yield, 80–85%, denoted as TMADT, TPADT and TBADT). In order to improve the catalyst's quality, both the crude catalysts TMADT and TBADT were re-crystallized in a mixture of MeCN and H_2O (MeCN:H_2O = 5:1), receiving the corresponding refined products. The W contents of both refined TMADT and TBADT measured by ICP-AES analysis were 68.76 and 54.80%, respectively, which were basically accordant with both the theoretical W contents. UV–vis spectral technique was used to evaluate the quality of these DT products and described as follows: Two charge transition (CT) bands of oxygen to tungsten at 325 and 267 nm, which are assigned to the structures of DT anion [59] and its twin $[W_5O_{16}]^{2-}$ [57], respectively, could be found in UV–vis spectra of these DT salts. The integral areas of such two CT bands could be calculated by ORIGIN 9.0 software and the ratio of the obtained both integral areas (R = $I_{325 \text{ nm}}/I_{267 \text{ nm}}$), defined as a relative intensity of DT structural band, was used to evaluate the quality or purity of DT salts. The calculated R values for these crude and refined DT products before and after visible illumination are listed in Table 1.

2.3. characterization of catalysts

Liquid UV–vis spectra (200–400 nm) of the samples in MeCN were obtained on UV-2450 spectrophotometer (Shimadzu, Japan) and their transmission FT-IR spectra in 400 to 4000 cm^{-1} recorded on a Nicolet Nexus 510 P FT-IR spectroscopy using a KBr disk. Photo-luminescence (PL) spectra of the samples were performed with a F-7000 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was obtained on an Escalab 250Xi with a monochromatic Al Kα source to text the elements on the surface of samples. The cyclic voltammetric (CV) measurements were conducted on an autolab electrochemical workstation

Table 1
R values of DTs obtained from liquid UV–vis spectra in Figs. 1,8, S1 and S3.

Catalyst	R values of DTs [a]		R values in MeCN-containing additive after irradiation for 12 h			
	Crude	Refined	Without [b]	H$_2$O	12 M HCl	H$_2$O + 12 M HCl
TMADT	1.092	1.100	1.031	1.051	1.015	1.047
TPADT	0.684	1.092	0.592	0.642	0.584	0.641
TBADT	0.608	1.090	0.516	0.562	0.499	0.560

[a] In pure MeCN before irradiation.
[b] In pure MeCN.

(EcoChemie, Holland). The used three-electrode con-figuration was composed of a glassy carbon working electrode (GCE, 3-mmdiameter disk), sheet of platinum foil counter electrode and KCl-saturated ca-lomel reference electrode (SCE). All the CV experiments were con-ducted at room temperature (20 °C). All potentials here are reported versus the SCE.

### 2.4. Evaluation experiments on photo-catalytic oxidation performance

Evaluation experiments for photo-catalytic oxidations were carried out on a self-assembly photo-reactor connected with a water-cooled condenser and an oxygen storage device (1 atm). A quartz glass tube built-in a 35 W tungsten-bromine lamp (with an UV light filter, light intensity, 535 mW cm^2) was installed in the center of the photo-reactor. The whole light illumination reaction was conducted under the closed conditions and its specific operating conditions and analysis method for the oxygenated products could be found in our recently publication [65].

3. Results and discussion

3.1. Characterization results of the catalysts

3.1.1. UV–vis spectrum

Fig. 1 is UV–vis spectra (200–400 nm) for the crude and refined samples of TMADT and TBADT in MeCN (Fig. S1 of Supporting In-formation (SI) gives the UV–vis spectra of crude and refined TPADT samples in MeCN). In that, two characteristic adsorption bands in 220–350 nm could be found in the UV–vis spectra of such two DT salts, which is accordant with the previous reports [55,56]. A band at 325 nm originates from a charge transition (CT) of oxygen to tungsten of four linear W—O—W bridge bonds in the DT structure [57]. Another band at 267 nm should be attributed to a CT process of oxygen to tungsten for the unstable structural subunit $[W_5O_{16}]^{2-}$ [59]. Notably, the crude TMADT exhibits a stronger DT structural band at 325 nm than the crude
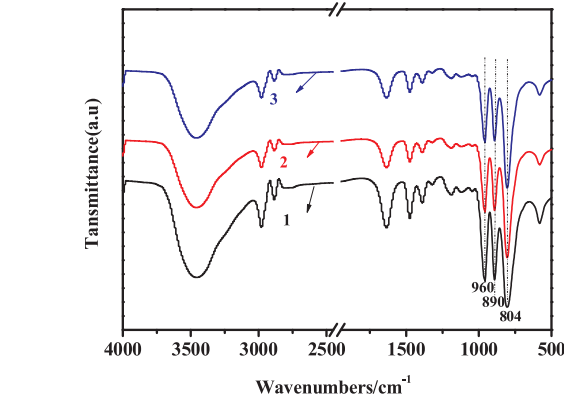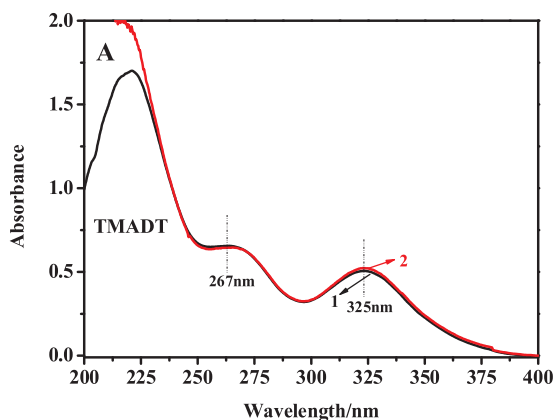
**Fig. 2.** FT-IR spectra of three DT salts. (1) TMADT; (2) TPADT; (3) TBADT.

TBADT (Fig. 1A vs B), indicating that the former has a higher quality than the latter. Here, the quality of DT salts could be roughly estimated according to the relative intensities (R = I$_{325\ nm}$/I$_{267\ nm}$) of their structural bands (A detailed definition of the R value can be found in experimental section). As can be seen from Table 1, the estimated R values for TMADT, TPADT and TBADT are 1.08, 0.684 and 0.608, re-spectively, presenting a gradual downward trend with increasing ca-tionic alkyl chain of DT salt. Notably, the R value of TBADT remarkably increases from 0.608 to 1.09 after re-crystallization (Table 1 and Fig. 1B), showing a significant improvement in its quality. Also, a si-milar improvement in quality is noticed upon the refined TPADT (Table 1 and Fig.S1). But such refined method is nearly invalid to im-prove the quality of TMADT (Curve 2 of Fig. 1A and Table 1). These findings indicate that the quality of DT salt is affected by its tetraalk-ylammonium cation and a high quality of TMADT can be synthesized directly using TMABr as a cation exchanger.

3.1.2. FT-IR spectra

FT-IR spectra of three DT salts shown in Fig. 2 are very similar to each other and present some very similar characteristic peaks in 500–4000 cm^{-1}, in consistence with previous study [65]. Among these peaks, three peaks located near 960, 890 and 804 cm^{-1} belong to stretching vibrations of W = O$_t$, W—O$_b$—W (O$_b$: corner-sharing bridged oxygen) and W—O$_e$—W (O$_c$: edge-sharing bridged oxygen), respectively, reflecting the structural character of DT anion. In addition, the several characteristic peaks located at 2959, 2867, 1479 and 1382 cm^{-1} should be relative to the tetraalkylammonium cations of DT salts.

3.1.3. XPS

X-ray photoelectron spectroscopy (XPS) is a forceful tool to in-vestigate the chemical states of the surface atoms in materials and this
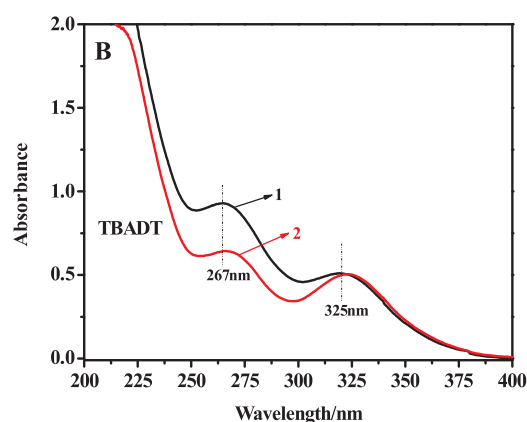
Fig. 1. UV–vis spectra of two representative TMADT (A, 5.5 × 10^{-6} M) and TBADT (B, 5.5 × 10^{-6} M) in MeCN. (1) crude product; (2) refined product.
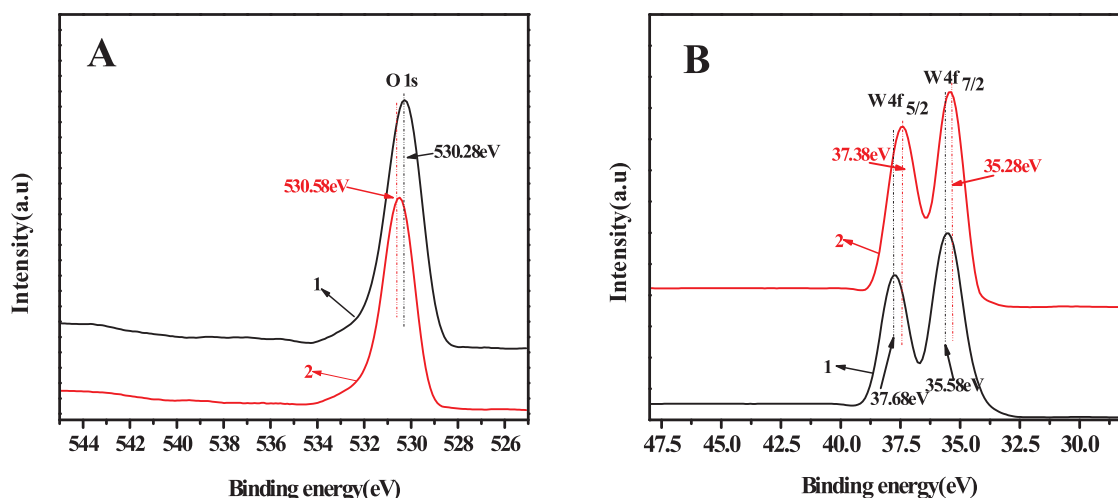
Fig. 3. High resolution XPS spectra for O 1 s (A) and W4f (B) in TMADT (curve 1) and TBADT (curve 2).

technique was used to check the influence of cations on the binding energies of tungsten and oxygen in DT salts. The survey XPS spectra of two typical TMADT and TBADT could be found in Fig. S2 and the corresponding high resolution XPS spectra for O and W atoms are shown in Fig. 3A and B, respectively. Fig. 3A shows that the binding energy (BE) of O1 s in TMADT is located at 530.28 eV and slightly lower than that of 530.58 eV in TBADT. In sharp contrast, the two BEs of W4f 5/2 and W4f 7/2 in TMADT appear at 37.68 and 35.58 eV, respectively, which are slightly higher than the corresponding two BEs at 37.38 and 35.28 eV in TBADT. (Fig. 3B). The XPS data supports that TMADT has a stronger bonding capacity among its O and W atoms than TBADT as the O electronegativity and W electropositivity of the former are higher than those of the latter, proposing that such a strengthened ionic bonding ability between W and O atoms should be conductive to improving the structural stability and redox capacity of TMADT but needs a high energy to realize its excitation, as supported by the accompanying UV–vis and PL spectra and CV measurements.

3.2. Photo-catalytic performance of tetraalkylammonium decatungstates

Table 2 lists data for the tetraalkylammonium decatungstate (DT) salts-catalyzed oxidation of cyclohexane with O_2 in MeCN under visible light irradiation. Entries 1–3 show that these DT salts (1.2% amount used), as previously reported by us [65], possess a low activity for this photo- reaction in pure MeCN, providing lower than 9% cyclohexane

conversion and cyclohxanone and cyclohxanol as the oxidative products. Among them, TMADT exhibits a very low conversion (ca. 1.6%) owing to its poor solubility in MeCN. And the conversion gradually increases from TMADT to TBADT, which should be due to a fact that the solubility of these DT salts is gradually enhanced with the increase of its cationic alkyl chain. The homogeneous photo-catalysis performance of these DT salts in pure MeCN is further checked *via* reducing their used amount to 0.1% and the obtained data are listed in parentheses of Entries 1–3. Contrary to the results described above, the conversion under homogeneous conditions gradually increases from 4.3% over TBADT to 7.3% over TMADT, which just corresponds to the quality of theses DT salts. Notably, the selectivity for cyclohexanone is continuously improved from TMADT to TBADT and such improved effect becomes more noticeable under a high catalyst dosage of 1.2%. This may be due to a fact that the hydrophobicity of the cage of DT salt is strengthened gradually with the increase of its cationic alkyl chain, thus increasing the opportunity that the primary oxidative product cyclohexanol is trapped in its strengthening hydrophobic cage and then oxidized to cyclohexanone. The following six experiments illustrate that the additive water (Entries 4–6) or 12 M HCl (Entries 7–9) can promote the present photo-catalysis oxidation to some extent and this boost effect is gradually weakened from TMADT to TBADT. It is worth noting that in the TPADT- and especially the TMADT-photo-catalyzed oxidations, the promoted effect of water is slightly superior to that of 12 M HCl, but the contrary result is noticed in the TBADT-photo- catalyzed

Table 2

Tetraalkylammonium decatungstates-catalyzed cyclohexane oxygenation with molecular oxygen under visible light illumination[a].

Entry	Catalyst	12 M HCl	MeCN	Water	Conv.	Selectivity of products (%)	
	(mmol %)	(mL)	(mL)	(mL)	mol%	Cyclohexanol	Cyclohexanone
1	TMADT	–	5.5	–	1.6 (7.3)[b]	40.2 (40.5)[b]	59.5 (59.8)[b]
2	TPADT	–	5.5	–	7.5 (5.1)[b]	35.5 (38.4)[b]	64.5 (61.6)[b]
3	TBADT	–	5.5	–	8.8 (4.3)[b]	32.8 (37.2)[b]	67.2 (62.8)[b]
4	TMADT	–	4.8	0.7	22.5	44.6	55.4
5	TPADT	–	4.8	0.7	18.0	33.8	66.2
6	TBADT	–	4.8	0.7	10.5	34.6	65.4
7	TMADT	0.1	5.4	–	17.3	24.8	75.2
8	TPADT	0.1	5.4	–	15.6	26.8	73.2
9	TBADT	0.1	5.4	–	12.5	30.2	69.8
10	TMADT	0.1	4.7	0.7	28.1	30.9	69.1
11	TPADT	0.1	4.7	0.7	25.9	36.1	63.9
12	TBADT[c]	0.1	4.7	0.7	20.2 (22.3)[c]	39.4 (36.7)[c]	60.6(63.3)[c]

[a] Cyclohexane (1.0 mmol), DT salts (0.012 mmol), O_2 (1 atm), 35 W of tungsten–bromine lamp, temperature (25 °C), time (12 h).

[b] Using low dosage of DT salt (0.0010 mmol).

[c] Data in parentheses were obtained using the re-crystallized TBADT.

oxidation. The adjusted effect of DT's cations on cyclohexanone selectivity in the presence of water is similar to that in pure MeCN, but the contrary rule is observed in the presence of 12 M HCl. Interestingly, simultaneously adding the above two additives can play a better synergistic promotion effect for these DT salts-photocatalyzed oxidation than only adding one of both (Entries 10–12 vs Entries 4–9) but does not affect the order of photo-activity of these DT salts. In this case, the high quality of TMADT can achieve ca. 28% conversion with 69% cyclohexanone selectivity. And the re-crystallized TBADT provides a slightly higher conversion than its crude one (see data in parentheses of Entry 12). By the way, the influence of DT's cations on these additives-promoted photo-catalysis oxidations under low used dosages (0.1%) also presents the aforesaid rules (see Table S1). These findings support that the photo-catalysis activity of DT salts should mainly depend on its quality. On the other hand, the polarity of DT cage, closely relative to the above additives-promoted DT photo-catalysis, relies on the alkyl cations surrounded around it and is gradually reduced from TMADT to TBADT, thus leading to a gradually increasing resistance that the above polar additives enter inside the cage of DT salts and weakening their promoted effect on the present photo-catalysis.

In the next experiments, the influences of other acidic additives and reaction parameters on the present photo-catalysis oxidation were further examined using the best TMADT as a catalyst. As shown in Table S2, these acidic additives examined exhibit the different degree of promoted effect on the visible light-triggered this oxidation in MeCN under the catalysis of TMADT. Among them, benzene sulfonic acid (PhSO$_3$H) as a strong organic acid shows the best promoted effect, achieving ca. 18% conversion. Two medium strong inorganic H$_3$PO$_4$ and H$_2$SO$_4$ solutions (10 M) also provide 16–17% conversion, but two weak acidic additives dichloroacetic acid and especially acetic acid only give ca. 13 and 11% conversions, respectively. This supports that the acidic strength of these additives is proportional to their promoted effects on the present photo-catalysis oxidation. Additionally, the above synergistic promotion effect is also noticed in the co-existence of these acids and water, but it doesn't catch up with that obtained in the co-existence of 12 M HCl and water.

Fig. 4 is the influence of catalyst concentration (0.1–2.5%) on the TMADT-photocatalyzed this oxidation. In that, cyclohexane conversion is rapidly enhanced from 5.5 to 28.1% as the concentration goes from 0.1 to 1.2 mol%, along with a slightly increase of cyclohexanone selectivity. Thereafter, the further increasing TMADT concentration is almost invalid to enhance the conversion owing to its solubility becoming worse. Fig. 5 illustrates that when the amount of water is enhanced from 0.3 to 0.7 mL, the conversion increases gradually from 14.5 to 22.1% and cyclohexanone selectivity decreases from 59.5 to 55.4%, indicating that the probability of further oxidation of
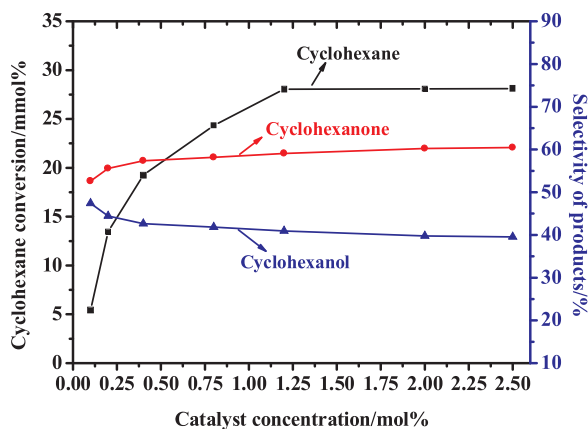

Fig. 5. Influence of water amount on the visible light-triggered oxidation of cyclohexane (1.0 mmol) by O$_2$ (reaction conditions: TMADT, 0.012 mmol; MeCN and water, 5.5 mL; illumination time, 12 h).

Fig. 6. Influence of HCl amount on the visible light-triggered oxidation of cyclohexane (1.0 mmol) by O$_2$ (reaction conditions: TMADT, 0.012 mmol; MeCN, 4.8 mL; water, 0.7 mL; illumination time, 12 h).

cyclohexanol inside the cage of TMADT is reduced owing to the increasing replaced effect of water to it. After that, the conversion rapidly descends with further increasing water amount, which should be due to the solubility of TMADT becoming worse. Fig. 6 displays that the conversion continuously and slowly ascends from 23.0 to 30.1% as HCl amount is enhanced from 0.1 to 1.2 mmol. However, an attempt to further increase HCl amount reversely results in a significant decrease in the conversion due to a decrease in the stability of catalyst [65]. Notably, cyclohexanone selectivity can be improved continuously from 54.0 to 65.2% as HCl amount increases from 0.1 to 1.2 mmol, which may be due to the enhancement of the oxidation capacity of DT anions through a strengthening protonated effect induced by HCl amount [65]. Fig. 7 illustrates that the conversion uninterruptedly and significantly goes up with prolonging irradiation time and achieves ca. 41.6% at 35 h. After that, an enhanced effect of the time on the conversion can be almost ignored. This is acceptable to that the selectivity for cyclohexanone as a further oxygenated product increases slightly with the time.

Finally, the TMADT-photocatalyzed selective oxidation of other substrates such as benzene, toluene (PhMe), ethylbenzene (EB) and benzyl alcohol (BA) by O$_2$ in MeCN was checked in the presence of water or 12 M HCl or the co-existence of both and the results are listed in Table 3. As previously reported by us [65], the present TMADT photo-catalysis system is still invalid to the oxidation of benzene whether the additives are present or absent (Entries 1–2), which should be due to the high C–H bond energy of benzene [68]. But other three aromatic compounds can be oxidized smoothly to the corresponding oxygenated products by the present TMADT photo- catalysis system and

Fig. 4. Influence of TMADT concentration on the visible light-triggered oxidation of cyclohexane (1.0 mmol) by O$_2$ (reaction conditions: MeCN, 4.7 mL; 12 M HCl, 0.1 mL; water, 0.7 mL; illumination time, 12 h).
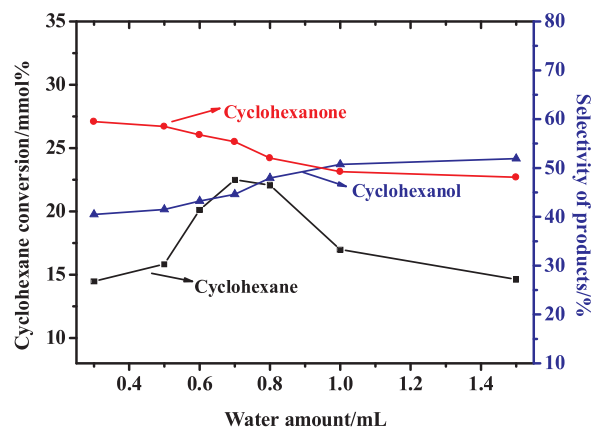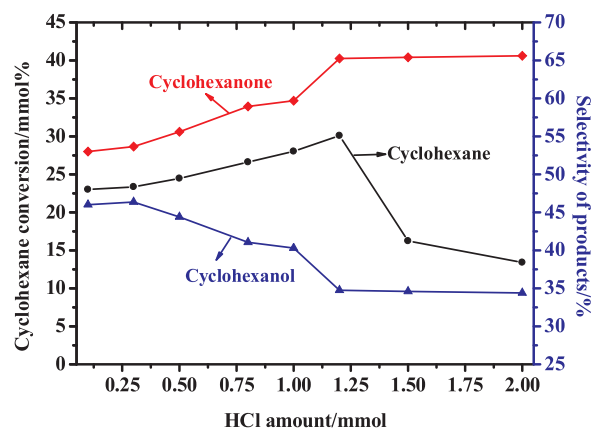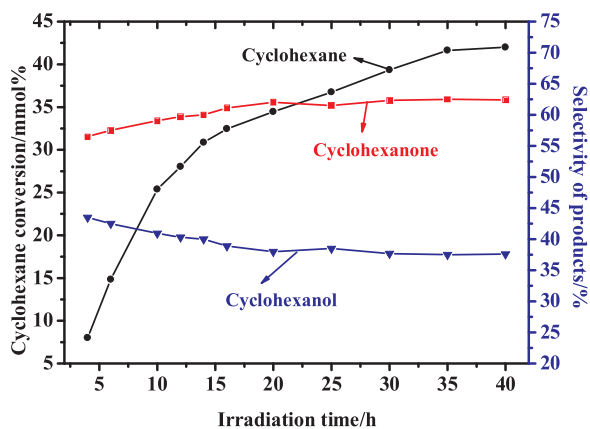
Fig. 7. Influence of illumination time on the visible light-triggered oxidation of cyclohexane (1 mmol) by O_2 (reaction conditions: TMADT, 0.012 mmol; MeCN, 4.7 mL; 12 M HCl, 0.1 mL; water,0.7 mL).

Table 3
Data for the oxidation of four aromatic substrates by O_2 in MeCN under TMADT catalysis and visible light illumination[a].

Entry	Substrate	Additive		Conv./mol %	Main products (Yield, mol%)
		HCl/ mmol	Water/mL		
1	Benzene	–	–	–	–
2	Benzene	1.0	0.7	–	–
3[b]	EB	–	0.7	12.5	α-PEA(2.8), ACP(9.7)
4[b]	EB	1.0	–	9.0	α-PEA(2.2), ACP (6.8)
5[b]	EB	1.0	0.7	19.0	α-PEA(3.4), ACP (15.6)
6	PhMe	–	0.7	6.1	BA(0.8), PhCHO (5.3)
7	PhMe	1.0	–	5.9	BA (1.2), PhCHO (4.7)
8	PhMe	1.0	0.7	14.8	BA (1.9), PhCHO (12.9)
9	BA	–	0.7	51.2	PhCHO (40.7), PhCOOH (10.5)
10	BA	1.0	–	48.9	PhCHO (44.1), PhCOOH (4.8)
11	BA	1.0	0.7	55.5	PhCHO (47.9), PhCOOH (7.6)

[a] Substrate (1.0 mmol), catalyst (0.012 mmol), acetonitrile (5.5 mL), O_2 (1 am), temperature (25 °C), time (12 h), using 35 W of tungsten-bromine lamp as visible light source.

[b] α-PEA and ACP presented phenethylalcohol and acetophenone, respectively.
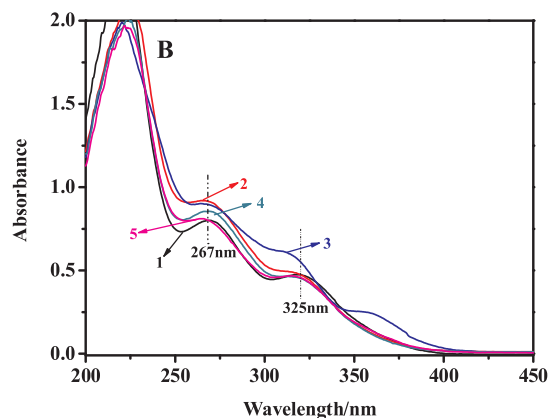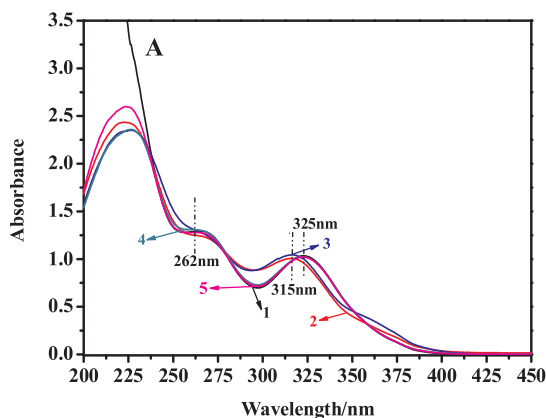
their reactivities follow an increasing sequence of BA > EB > PhMe, which is accordant with their gradually reducing side chain C–H bond energies [68]. These oxidative products include BA and benzaldehyde (PhCHO) for PhMe, α-phenethylalcohol (α-PEA) and acetophenone (ACP) for EB, PhCHO and benzoic acid (PhCOOH) for BA. The promoted effect of the additives on the photo-catalysis oxidation of these substrates is very similar to that above mentioned on the TMADT-photocatalyzed cyclohexane oxidation. The high quality of TMADT exhibits a good photo-catalysis activity for the oxidation of two alkyl aromatic hydrocarbons and can achieve 14.8% toluene conversion and 19.0% EB conversion under the co-promotion of 12 M HCl and water, which is obviously superior to the corresponding 3.8 and 12.3% results obtained in our previously reported TBADT photo-catalysis system [65].

3.3. Study on the mediated mechanism of the additives on DT salts

3.3.1. UV–vis spectra

In order to explore the reasons that the above additives are able to boost the photo-catalyzed activity of these DT salts for the selective oxidation of inert hydrocarbons by O_2 in MeCN, the UV–vis spectra of these DT salts in MeCN containing different additives were recorded after 12 h of uninterrupted visible light irradiation. As observed in Fig. 8A, the structural band of TMADT at 325 nm in pure MeCN slightly decays and takes place a slight blue-shift after illumination of 12 h, along with an uplift of the traces in 340–380 nm and especially 310-270 nm (Curves 2 vs 1 in Fig. 8A). Furthermore, such spectral changes become slightly obvious in the presence of 12 M HCl (Curve 3). On the contrary, in the presence of water or in the coexistence of water and 12 M HCl, 12 h of illumination does not lead to perceptible changes in the UV–vis spectrum of TMADT at 250–350 nm (Curve 4 and 5). This implies that TMADT in pure MeCN is not too stable under the condition of simulating real light reaction and its stability seems to further decrease in the presence of 12 M HCl but can be improved significantly in the presence of water whether the additive 12 M HCl is absent or present. Also, Yue et.al [67] previously reported that DT anion in some solvents (including MeCN) can be degraded to a unstable subunit $[W_6O_{19}]^{2-}$ under heating and this transformation process may be remarkably restrained in the presence of water, indicating that this unique inhibition of water on the degradation of DT anion should be responsible for its stabilization on DT anion. The additive HCl probably weakens the W−O bonds of DT through its protonation [69], thus leading to reduced the stability of DT anion. The exerted effects of the additives on the stability of TPADT and TBADT under illumination are similar to those above mentioned (See Fig. S3 and Fig. 8B, respectively),

Fig. 8. UV–vis spectra (200 nm–400 nm) of TMADT (9.5×10^{-6} M) (A) and TBADT (5.5×10^{-6} M) (B) in MeCN solvent containing 1.0 mmol cyclohexane. (1) The system in a pure MeCN (5.5 mL) without illumination; (2) The system 1 after irradiating for 12 h; (3) The system in MeCN (5.4 mL) and HCl(12 M, 0.1 mL) after irradiating for 12 h; (4) The system in MeCN (4.8 mL) and H_2O (0.7 mL) after irradiating for 12 h; (5) The system in MeCN (4.7 mL), HCl(12 M, 0.1 mL) and H_2O (0.7 mL) after irradiating for 12 h.

but the structural degradation of TPADT and especially TBADT in pure MeCN is faster than that of TMADT under illumination and such degradation is accelerated significantly in the presence of 12 M HCl, further supporting that the structural stability of DT anion is influenced by its counter cations and gradually decreases from TMA^+ to TBA^+ ion. In addition, the stabilized effect of water on the structure of DT anion becomes weaker on TPADT and especially TBADT than TMADT owing to a decrease in the hydrophilicity of such two DT salts. Additionally, the quality of these DT salts was checked using the R values obtained from the UV–vis spectral curves in Fig.8 and Fig. S3. As shown in Table 1, these R values clearly reflect the above influence rules of the reaction media on the stability of these DT salts under light illumination.

3.3.2. Cyclic voltammograms (CVs)

As TBADT has much better solubility in MeCN than TMADT, Firstly, the cyclic voltammograms (CVs) of its high concentration (2.6×10^{-2} M) in MeCN were studied under with or without the additives and the measured results are shown in Fig. S4. The main conclusions summarized from Fig. S4 are as follows: i) The oxidative ability of TBADT in MeCN becomes weak in the existence of water but strong in the presence of 12 M HCl owing to the protonation of HCl [69]. And ii) a redox recycling between its W^{6+} and W^{5+} ions in MeCN can be improved under the action of water or 12 M HCl.

Next, the CV measurements for the low concentration (2.6×10^{-3} M) of these DT salts in MeCN were conducted with the help of additive 12 M HCl and its mixture with water and the recorded CVs are shown in Fig. 9 (the CV curves of TPADT are given in Fig. S5). Notably, under the exertion of such two additives, a pairs of quasi-reversible W^{6+}/W^{5+} redox waves for low concentration of TBADT salt shows very similar changes to that for high concentration of TBADT although its redox potential presents different degree of shift (Fig. 9 vs Fig. S4), but the difference between its oxidative and reductive peaks in the co-existence of 12 M HCl and water is 0.047 V and significantly smaller that (0.355 V) in Fig. S4, indicating that TBADT with low concentration has a good redox cycling under the action of this acidic solution. It is seen from Fig. 9 and Fig. S5 that the redox potential for this pair of redox waves is influenced by the cations of DT salts and follows an increasing sequence of TMADT (-0.0045 V) > TPADT (-0.016 V) > TBADT (-0.031 V) in the presence of 12 M HCl. Notably, the redox potentials of TMADT, TPADT and TBADT in the co-existence of 12 M HCl and water are -0.0565, -0.065 and -0.0795 V, respectively, also presenting the above increasing regularity from TBADT to TMADT. In addition, three DT salts show a little difference to each other (no more than 10 mV) for the peak to peak separation of their CV curves in the co-existence of

12 M HCl and water. These findings indicate that the oxidative capacity of DT anion is also relative to its counter cations and gradually strengthened from TBADT to TMADT, in consistence with the previous report that the oxidative ability of DT anion is gradually strengthened with reducing the chain of tetraalkylammonium cations in DMF [70]. On the other hand, an improvement in the redox recycling of DT anion is mainly dominated by the additives and the exerted effect of its counter cations on such improvement should be inappreciable.

3.3.3. Photoluminescence (PL) spectra

Photoluminescence (PL) spectroscopy is usually used to study the recombination probability of photo-generated electron-hole pairs, thus testing the stability (or lifetime) of the photo-excited state closely relative to photo-catalytic efficiency [71,72]. However, to the best of our knowledge, the PL properties of DT salts in MeCN and especially in the presence of the above additives are rarely investigated to date. Herein, this spectral technique is firstly applied to the DT photo-catalysis system with or without the additives. As shown in Fig. 10 and Fig. S6, a strong and broad PL signal in 350–550 nm can be generated when these DT salts in MeCN are excited by light of 320 nm, its intensity is almost unaffected by the cations of DT salts, but its noticeable blue-shift (about 45 nm) can be observed upon TMADT, indicating that TMADT needs a higher energy to realize its excitation than TBADT, which is consistent with the above XPS results. The additive water can slightly enhance the PL intensity of these DT salts, but does not cause a displacement of their PL signals. Such enhanced effect of water on PL intensity is not nearly influenced by the cations of DT salts when PL spectra were measured after 300 s of adding water, but before that, the PL signals of these DT salts gradually increase with the delay of measurement time and finally reach maximum after 150 s for TMADT, 180 s for TPADT or 270 s for TBADT (Fig. S7). These findings support that the additive water probably exerts a weak hydrogen bond interaction on DT anion, which can cause the photo-excited state of DT anion become slightly unstable. And the water-mediated such interaction can be accelerated gradually from TBADT to TMADT owing to an increase in hydrophilicity of DT's cations. In contrast to the above results, the additive 12 M HCl can weaken the PL signals of these DT salts to some extent and its weakened effect on PL intensity is more noticeable upon TMADT. In addition, the delay of measurement time does not result in an obvious decrease in the PL signals of TMADT and TBADT (Fig. S8). These findings support that 12 M HCl shows a strong interaction with DT anion by its protonation, which enhances the stability of DT photo-excited state and thereby improves the photo-catalysis efficiency. Furthermore, the stabilized effect of 12 M HCl on DT photo-excited state is affected by the cations of DT salts and strengthened significantly in TMADT due to its strong protonation ability, as supported by the above XPS and photoreaction results. Additionally, under the co-existence of the above two additives, the PL signals of these DT salts are only slightly weakened, indicating that the photo-excited state of DT anion is basically insensitive to the mixture of water and 12 M HCl as the opposite effects of such two additives on it are almost offset.

We can further draw the following conclusions from the above characterization results: i) The additives water and 12 M HCl can influence the stability and redox property of DT anion and the lifetime of its photo-excited state through weak hydrogen bond interaction and strong protonation, respectively. The most important contribution of water on DT photo-catalysis is able to improve the stability of DT anion under light irradiation, the main functions of 12 M HCl can enhance the oxidative capacity and redox cycle of DT anion, as well as improve the stability of its photo-excited state, while the co-existence of such two additives can well combine their respective promotion effects on photo-catalysis. And ii) the above promotion effects of two additives on DT photo-catalysis are affected by the cations of DT salts and can be gradually strengthened with the shortening of its cationic alkyl chain, possibly due to an increase in the hydrophilicity of DT anion, enhancing the interactions with the two additives.
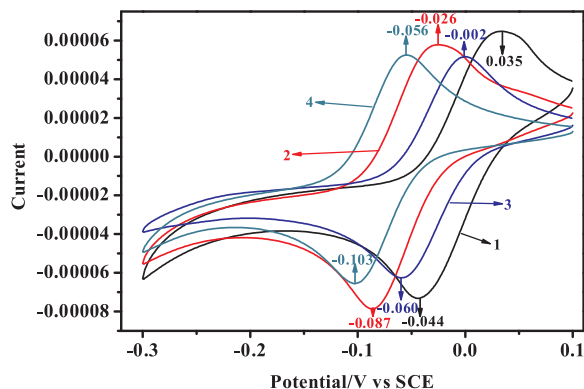

Fig. 9. Cyclic voltammograms (CVs) of two DT salts (2.6×10^{-3} M) in MeCN. 1: TMADT in mixed solvents HCl (12 M, 1.0 mL) and MeCN (9.0 mL) 2: TMADT in mixed solvents HCl (12 M, 1.0 mL), H_2O (0.5 mL) and MeCN (8.5 mL); 3: TBADT in mixed solvents HCl (12 M, 1.0 mL) and MeCN (9.0 mL); 4: TBADT in mixed solvents HCl (12 M, 1.0 mL), H_2O (0.5 mL) and MeCN (8.5 mL).
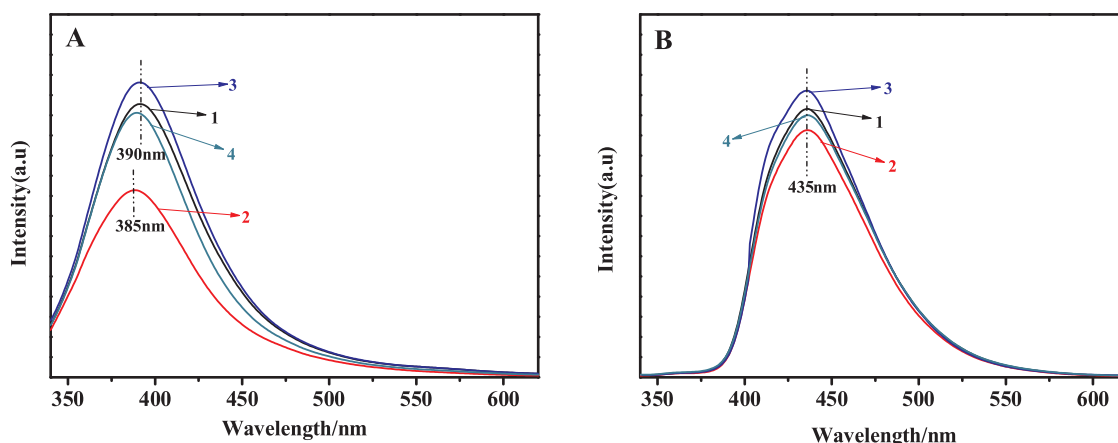
Fig. 10. PL spectra of TMADT (2.0×10^{-4} M) (A) and TBADT (2.0×10^{-4} M) (B) in MeCN. 1: A pure solvent MeCN (5.5 mL); 2: The mixed solvents HCl (12 M, 0.1 mL) and MeCN (5.4 mL); 3: The mixed solvents H_2O (0.7 mL) and MeCN (4.8 mL); 4: The mixed solvents H_2O (0.7 mL), HCl (12 M, 0.1 mL) and MeCN (4.7 mL).

4. Conclusion

To summarize, for the first time we have found that the quality, redox property and excited state of DT anion are influenced by its tetraalkyl cation and the additives, which can play important roles in it-photocatalyzed the oxidation of some inert hydrocarbons by O_2. The use of TMA^+ as a counter cation can directly synthesize the high quality of TMADT, the additive water mainly helps to stabilize the structure of DT anion under light illumination and the additive 12 M HCl can enhance the oxidative capacity and redox recycling of DT anion, as well as stabilize its excited state. Furthermore, these favorable effects of both additives on the improved photo-catalysis activity of DT anion become more outstanding upon TMADT and can be well combined together under both co-existence. As a result, a high quality of TMADT can efficiently catalyze the visible light-triggered oxidation of cyclohexane, toluene and ethylbenzene by O_2 in MeCN under the joint action of water and 12 M HCl. Having these interesting findings, we will be interested to exploit new strategies that can significantly improve the photosensitive activity of DT anion by doping transition metals or carbon quantum dots.

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2018.09.099.

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